MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS 1963 A

THERMOPHYSICAL PROPERTIES RESEARCH LABORATORY

AD-A134564

TPRL 314A

SPECIFIC HEAT OF OCTAHYDRO - 1,3,5,7 -
TETRANITRO - 1,3,5,7 - TETRAZOCINE (HMX)

A Special Report to AFOSR

by

L.G. Koshigoe, R.L. Shoemaker and R.E. Taylor

October 1983

School of Mechanical Engineering

Purdue University, West Lafayette, Indiana

83 11 04 060

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. *A134564*	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Specific Heat of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine (HMX)		**5. TYPE OF REPORT & PERIOD COVERED** Special Report (Scientific) October - 1983
		6. PERFORMING ORG. REPORT NUMBER TPRL 314A
7. AUTHOR(s) L.G. Koshigoe, R.L. Shoemaker and R.E. Taylor		**8. CONTRACT OR GRANT NUMBER(s)** F 49620-81-K0011
9. PERFORMING ORGANIZATION NAME AND ADDRESS Thermophysical Properties Research Laboratory Purdue University West Lafayette, IN 47907		**10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS** AFOSR F 49620-81-K0011 258-53-12885
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research Bolling AFB, D.C. 20332		**12. REPORT DATE** October 1983
		13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Air Force Office of Scientific Research Bolling AFB, D.C. 20332		**15. SECURITY CLASS. (of this report)** UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

TPRL Publication (DTIC source code 411787) 2595 Yeager Road, CINDAS Bldg., West Lafayette, IN 47906

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Specific Heat
HMX

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The specific heat of octahydro-1,3,5,7-tetranitrol,3,5,7-tetrazocine (HMX) has been studied with a Differential Scanning Calorimeter from 294-486°K. Measurements were made on both small pieces of single crystals and on a powdered blend of HMX. In both cases, the specific heats of beta and delta phases and also of partially decomposed HMX were determined. The results show that the specific heat values for the two phases are nearly the same. Differences in the specific heat values for the single crystals, powdered, and partially decomposed samples are small and all like within a band of 6%. The values for the single crystals
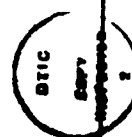
DD FORM 1 JAN 73 **1473**

#20 (continued)

are the lowest; for the powdered blend, intermediate; and for the
partially decomposed, highest. In the case of the single crystals
versus the powder, the values are within the combined experimental
error of 3%. ——

A-1

TPRL 314 A

SPECIFIC HEAT OF OCTAHYDRO - 1,3,5,7 -
TETRANITRO - 1,3,5,7 - TETRAZOCINE (HMX)

A Special Report to AFOSR

by

L.G. Koshigoe, R.L. Shoemaker and R.E. Taylor

October 1983

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICIES

INTRODUCTION

Knowledge of the specific heats of rocket propellants, especially at higher temperatures where significant decomposition occurs, is necessary for understanding various physical processes which occur in the combustion of these propellants. When the specific heats are combined with the thermal diffusivities and densities of the propellants, then the thermal conductivities can be calculated. Because of the small sample sizes and the rapidity of the measurements, this approach is preferred over direct thermal conductivity determinations.

As a step towards the goal of understanding the nature of heat transfer in a particular propellant, namely octahydro - 1,3,5,7 - tetranitro - 1,3,5, 7 - tetrazocine (HMX), the specific heat was determined by the use of a Perkin-Elmer Model DSC-2 Differential Scanning Calorimeter (DSC). Both small pieces of single crystals and a powdered blend of HMX were studied. Previous determinations of the specific heat of HMX were made by the use of an ice calorimeter (1) and Perkin-Elmer Model DSC-1B Differential Scanning Calorimeters (2), (3), and (4). From accurate specific heat values over a reasonable temperature range, values for the non-decomposed material can be safely extrapolated to higher temperatures. This will give usable values into the combustion temperature range, where the greatest interest lies.

In addition, the material present at the combustion temperature consists of HMX and decomposition products (5), so it is important to know the effects on specific heat due to decomposition products intermixed in the HMX lattice.

Specific heat results were also obtained for a sapphire standard immediately following the HMX runs, to check the experimental error. The sapphire

used was approximately the same mass as the HMX samples to insure comparable errors. Results for sapphire rerun typically fell within 1.5% of the previous values.

EQUIPMENT

A Perkin-Elmer Model DSC-2 Differential Scanning Calorimeter was used for the specific heat determinations. Slight modifications were made to the sample enclosure by using a Flow-Through Cover (Perkin-Elmer accessory 319-002), which decreases the amount of contamination to the enclosure due to decomposition or vaporization of the sample. Nitrogen gas was continuously allowed to pass through the enclosure and cover, thus purging out most evolving gases from the sample.

The DSC measures the differential power required to keep a sample's temperature rising at a chosen rate when compared to that of a reference. When a standard such as sapphire is measured in addition to the sample, then the calculation of specific heat is greatly simplified. The defining equation for specific heat at constant pressure is $C_p = \frac{1}{M}\frac{dq}{dt}$ where M denotes the sample mass, dq the differential heat absorbed, and dt the differential temperature change. Given known specific heat values for the standard material (sapphire), and from measurements of the standard's and sample's masses and differential power requirements obtained by raising their temperatures at the same rate as that of the reference, the specific heat of the sample may then be calculated by

$$C_{psam} = C_{pstd} \frac{M_{std}}{M_{sam}} \left[\left(\frac{dq}{dt}\right)_{sam} \Big/ \left(\frac{dq}{dt}\right)_{std} \right].$$

All measurements of HMX were made using sapphire as the standard.

Data retrieval and analysis were completely controlled by a digital data acquisition system. This minimized errors caused by human interaction and also significantly reduced total time spent for data analysis.

SAMPLE PREPARATION

Little sample preparation was required prior to the DSC measurements. Relatively large single crystals of HMX were remotely cleaved, until small enough pieces were obtained to fit into the sample pans (diameter $\simeq$ 5mm, thickness $\simeq$ 1mm). It was found that the samples needed to be as massive as possible to obtain good repeatability. Typical samples masses were about 17 mg. The single crystals were grown and furnished by Boggs, Price, Zurn, Derr and Dibble (6), and as stated in their paper, were believed to have been of very high purity. Their electrochemical analysis showed no evidence of RDX (hexahydro - 1,3,5 - trinitro - s - triazine)to an accuracy of < 0.1%.

Powder samples consisted of a blend of various particles sizes (see Table 1) and are 99.7% pure HMX. In this case sample sizes of about 19 mg. were typical.

In both the single crystals and powdered blend samples, the DSC pan lids were crimped onto the sample pans using a DSC crimping press.

Partially decomposed samples were prepared by heating a single crystal or powdered blend sample up to approximately 510°K in a furnace, and maintaining it at that temperature until sufficient decomposition was apparent. If a sample had lost one-eighth or greater of its mass, it was considered to

have undergone sufficient decomposition to assume that a significant portion of the remaining material consisted of decomposition products. Checks were made on mass losses every few minutes. It was assumed that the mass loss was caused by decomposition and volatilization of gaseous products, and volatilization of higher vapor species. However, it was not known how much of the remaining material consisted of HMX and how much was decomposition products. It was assumed that a significant amount of decomposition products were retained in the sample. Evidence of the validity of this assumption will be given later.

RESULTS AND DISCUSSION

Specific heat results are shown in Figure 1 for the single crystal and powdered blend HMX samples at a heating rate of 5°K/min. These results are for the β phase only and were obtained over a range of 294-445°K. Differences in the single crystal and powder specific heats were small. The maximum deviation between the two was approximately 3%. The powder results tended to be biased slightly upwards from that of the single crystal. The difference is at the limit of the combined experimental error.

Several samples were measured using heating rates other than 5°K/min (i.e., 2.5°K/min and 10°K/min) to check on whether uniform heating of the samples was maintained. No biasing in results was observed over a factor of four variation in heating rates, so it could be assumed that specific heat results were insensitive to any existing temperature gradients. In addition, several samples were tested more than once, to observe the affects on specific heat values with repeated heatings. No apparent change was seen upon rerunning

the samples.

In addition to the specific heat results obtained for the β phase in this work, the results of Velicky, Lenchitz and Beach (1) using an ice calorimeter and those of Krien, Licht and Zierath (2), Rylance and Stubley (3), and Wilcox (4) using DSC-1Bs are shown in Figure 1. Differences in all cases fell within a band of 6% of each other, which is very good given the inherent experimental and calculational errors in each case.

The temperature range over which δ phase data past the transformation could be obtained was small due to appreciable exothermic effects accompanying sample decomposition. It was found that accurate specific heat values in the δ phase (beyond the transformation) could only be obtained from 472 to 486°K (not shown). Since the δ phase results could only be obtained over a very short temperature range above the phase transformation, other techniques were sought for extending this range. It was apparent that after a sample had been taken below the transformation temperature, the reverse transformation (i.e., δ to β) occurred very slowly. In fact, it could take hours or weeks to completely transform back to β phase, depending on the sample's purity and crystallinity (5). Taking advantage of this fact allowed for δ phase results to be obtained at temperatures below the transformation temperature, thus extending the range of valid δ phase specific heat data. Sample temperatures were normally lowered to 400°K immediately following completion of the phase transformation, and then the samples were run again to determine their specific heats from 410-485°K. See Figure 2 for comparisions of the differential power absorbed during a run through the transformation and then a run immediately following cooling

to 400°K. As seen, there is only a small difference between the amplitudes
(thus implying equivalent specific heats). Also it is apparent that no
tranformation peak occurred in the second run, thus implying the sample
remainined in the δ phase over the entire temperature range for this run.
Results for the δ phase could not be obtained at a temperature lower than
approximately 400°K due to partial transformation back to the β phase during
subsequent runs. Also shown in Figure 2 is the empty pan reference run.

Figure 3 shows the specific heat resul obtained in the δ phase
versus those of references (2) and (3). In is case the powdered blend
results were slightly higher than those of i ngle crystal (as they were
for the β phase), but both were within 9% of the results obtained by Rylance
and Stubley (3). Krien, Licht and Zierath (2) obtained results which were
significantly larger than the present results (maximum deviation $\simeq$ 14%).
Confidence exists in the present results due to good repeatability, and also
due to good sapphire results obtained immediately following the HMX runs.

Comparisons between the specific heat results obtained in the β and
δ phases showed that the specific heats of the two phases are similar.
This would be expected since specific heat is relatively insensitive to
changes in crystal structure, and in fact, is also fairly insensitive to
changes in concentrations of similar materials. Concentration changes
exist due to decomposition and evolution of the gaseous products, but these
are small at the transformation temperature. Therefore the specific heat

values for the two phases would be expected to be in good agreement.

The specific heats of samples which had undergone significant decomposition in a separate oven were measured from 315 to 445°K. No results could be obtained beyond this range due to excessive decomposition occurring during the run. Since specific heat data could not be obtained beyond this range due to large decomposition effects, it is believed that sufficient decomposition products had been retained in the sample lattice and were catalyzing further decomposition (7). No β to δ phase transformation was observed for the partially decomposed samples unless the samples were stored for several days before checking again. For the powder, the transformation was small, and in the case of the single crystal, it was almost non-existent, as seen by the use of the DSC. This gives additional evidence that the samples contained significant portions of decomposition products. Thus, the values obtained from these runs could be assumed to be for a mixture of HMX and decomposition products. Both single crystal and powdered HMX were measured in this way.

Figure 4 compares the results for the partially decomposed single crystal and powder samples to those for the parent materials. The specific heats of the partially decomposed samples tended to be shifted upwards by a few percent. Since significant portions of the samples had decomposed, and since large portions of the decomposed material had vaporized, the change in chemical makeup of the remaining material could have caused an increase in specific heat. Note that the partially decomposed powder results tended to be slightly above those of the partially decomposed single crystal. The maximum deviation between the single crystal and decomposed single crystals was 5%, whereas for the powder versus the decomposed powder, it was

4%. While the difference is within the combined experimental error, the average increase appears to be slightly greater for the single crystal than for the powder, and this may be attributed to decomposition products being retained in the single crystal lattice to a much greater extent than in the case of the powder, due to its larger particle size (7).

The β to δ transformation resulted in an endotherm near the transformation temperature. In addition to the normal β to δ phase transormation endotherm, extra endotherms were observed at other temperatures in some cases. These additional endotherms were sometimes seen during a first run of a sample, but were most often seen after repeated heatings. They typically occurred between 490-500°K, although on occasion they were observed at lower temperatures. The causes could be due to : (1) non-uniform heating because of poor thermal contact between portions of the samples and the pans they were contained in or because of an increase in intergranular resistance after transformation due to a decrease in sample density; (2) creation of nucleation sites after partial decomposition or by retention of δ-HMX in the lattice from previous runs, thus causing a transformation to occur at lower temperatures; or, (3) an addition polymorphic conversion other than β to δ. Cady and Smith (10) observed that sometimes α-HMX is formed along with β-HMX during the β to δ phase transformation, and than α would undergo conversion to δ upon additional heating. Probably the first and second possibilities were responsible for the conversion in samples which had already been heated, but the third could explain the endotherms in virgin samples.

CONCLUSIONS AND SUMMARY

Specific heat results for the β phase of HMX have been obtained for both single crystals and a powdered blend from 294 to 445°K. The powdered blend samples had specific heats which were biased upwards from that of the single crystals, with a maximum deviation of about 3%. This might be due to impurities, but is at the limit of the combined experimental error. No differences in results were obtained by using various heating rates for either case. Literature values (1) - (4) for the specific heat of β-HMX are in good agreement with those found in the present work, and differ at most by about 6% from either the single crystals or powdered blend results.

In addition to the β phase results, determinations of the specific heat of HMX were also made in the δ phase. Again, measurements were made on both single crystal and powdered blend HMX. Data beyond the normal transformation temperature (i.e., β→δ transition) were obtained from 472 to 486°K. Also, due to the sample's hysteresis for the reverse transformation (i.e., δ→β) after cooling below the transition temperature, results could be obtained in the δ phase over an extended range of 410 to 485°K. Differences in results for the two ranges were within the experimental error. The maximum differences between the present results and those reported in references (2) and (3) are 14 and 9%, respectively. Additional calibration runs using a NBS sapphire standard were made immediately following the present runs and were generally within ±1.5% of the NBS values.

Comparison between the β and δ phase specific heat values show the two have similar dependences on temperature and can be assumed to be the same within ±1%. Thus, specific heat as a function of temperature for HMX in both the β and δ phases is known from 294 to 486°K within an experimental uncertainty of ±1.5%.

Samples which had undergone partial decomposition and contained signi-
ficant portions of decomposition products were also studied. Values of the
specific heats for these samples were found to be slightly larger, with the
partially decomposed single crystal deviating from the undecomposed material
by about 5% and the powdered blend deviating from the undecomposed material
by 4%. The biasing effect would be expected to be small since the decom-
position products retained in the HMX lattice would be of a similar nature
to that of pure HMX. Note that the somewhat greater amount of biasing seen
for the single crystals than for the powdered blend could be explained by
increased retention of decomposition products in the lattice of the single
crystal (7). From the present results, it may be concluded that the
specific heat of combinations of HMX and its decomposition products will
have a similar specific heat to that of undecomposed material.

The temperature of initiation of the tranformation of HMX from the β
to δ phase was found to occur at 453°K for the single crystals and 460°K
for the powdered blend. These results are higher than those seen by others (5)
and (8) using different equipment and techniques, but similar to that found
by Hall (9) using a DSC-1.

From the specific heat values obtained for both the β and δ phases of
HMX, and from determinations of their corresponding thermal diffusivities,
values for the thermal conductivities may then be calculated (given the
density of the material). Studies are underway to determine the thermal
diffusivity of HMX in both the β and δ phases, and to determine the effects

of partial decomposition. This information is important since partially decomposed HMX is the existing form at the combustion temperature (5).

Tabulated results for the data obtained in this study are given in in the Appendicies.

Table 1   Purity and blend information for
HMX powdered blend samples

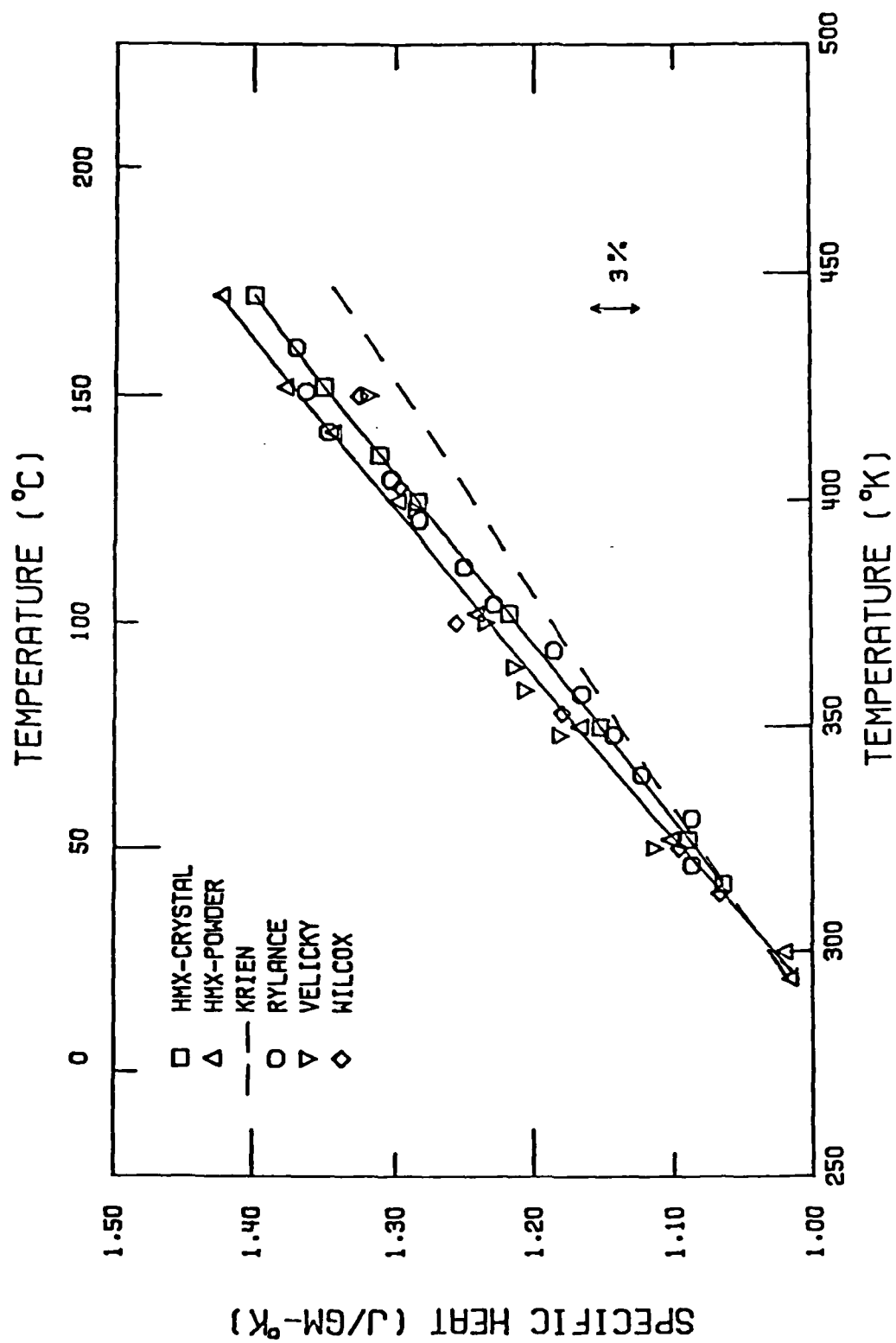| Material	Holston lot number	Particle size (μm)	Percent occupying blend	Percent HMX (purity)
HMX	5486	18.9	50	99.7
HMX	7016	6.0	30	99.7
HMX	7016	3.3	20	99.7

Figure 1. Specific heat of single crystal and powdered blend beta-HMX against literature results
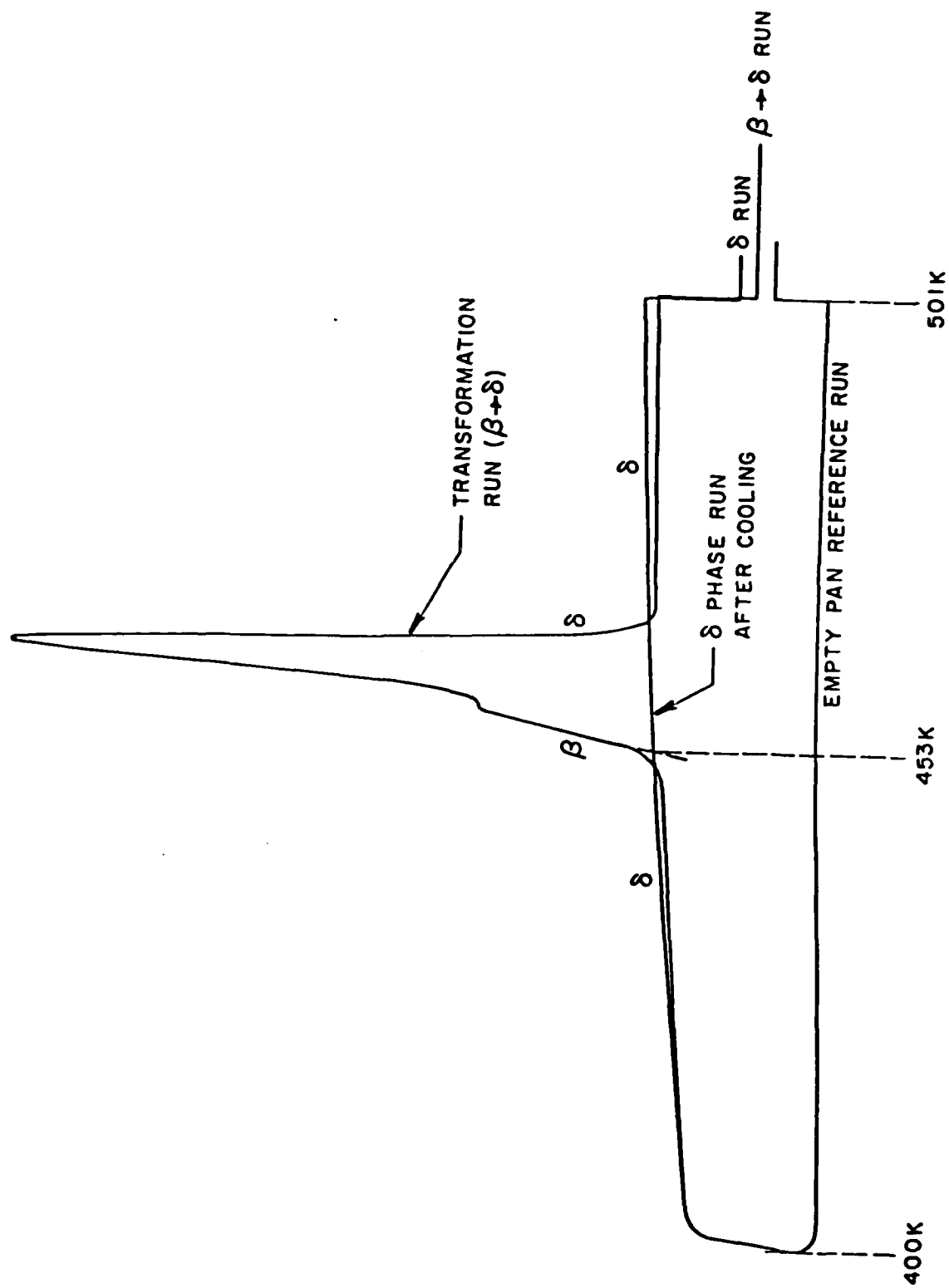
Figure 2. The DSC x-y recorder trace for single crystal HMX through the beta to delta phase transformation and also for the delta phase run
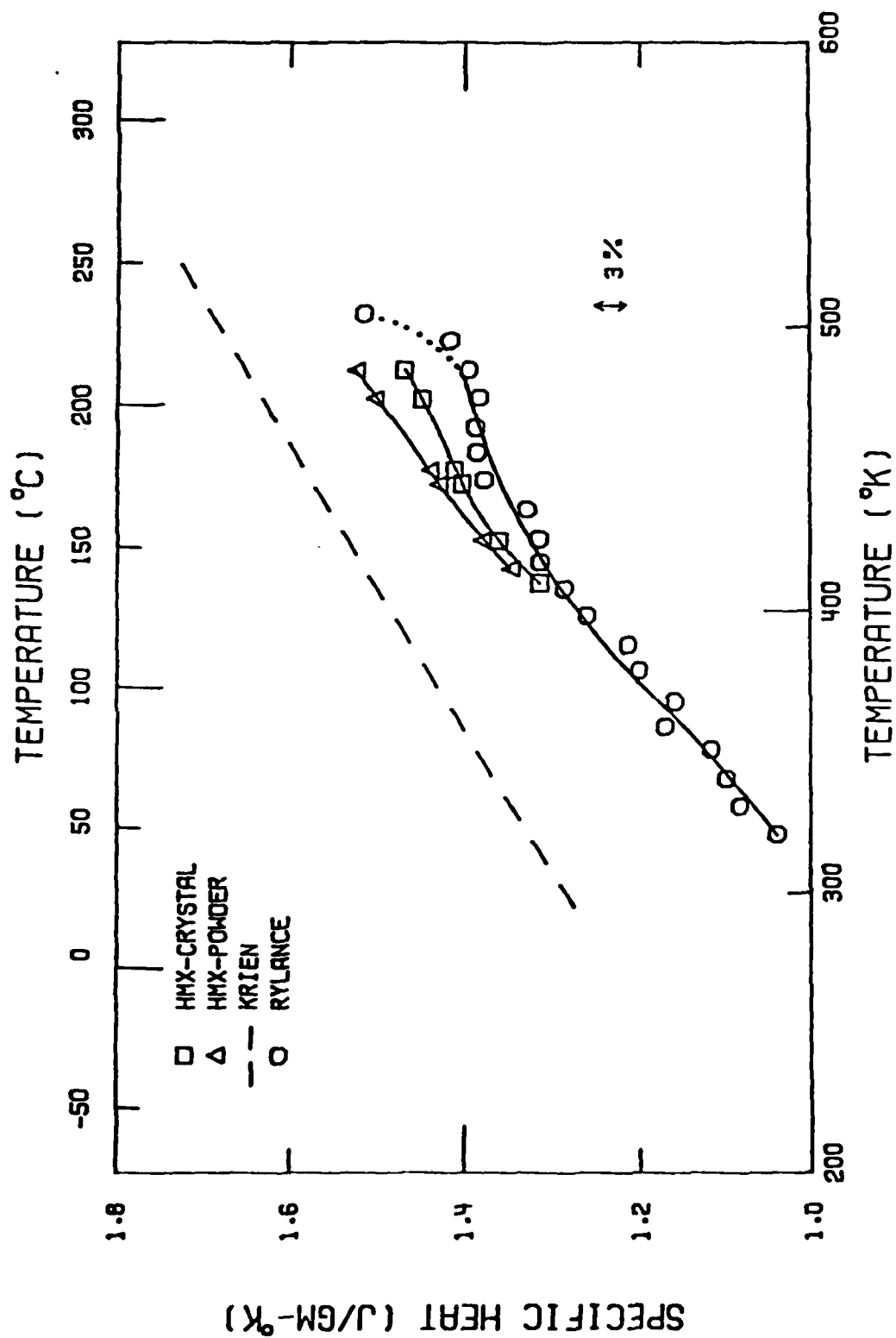
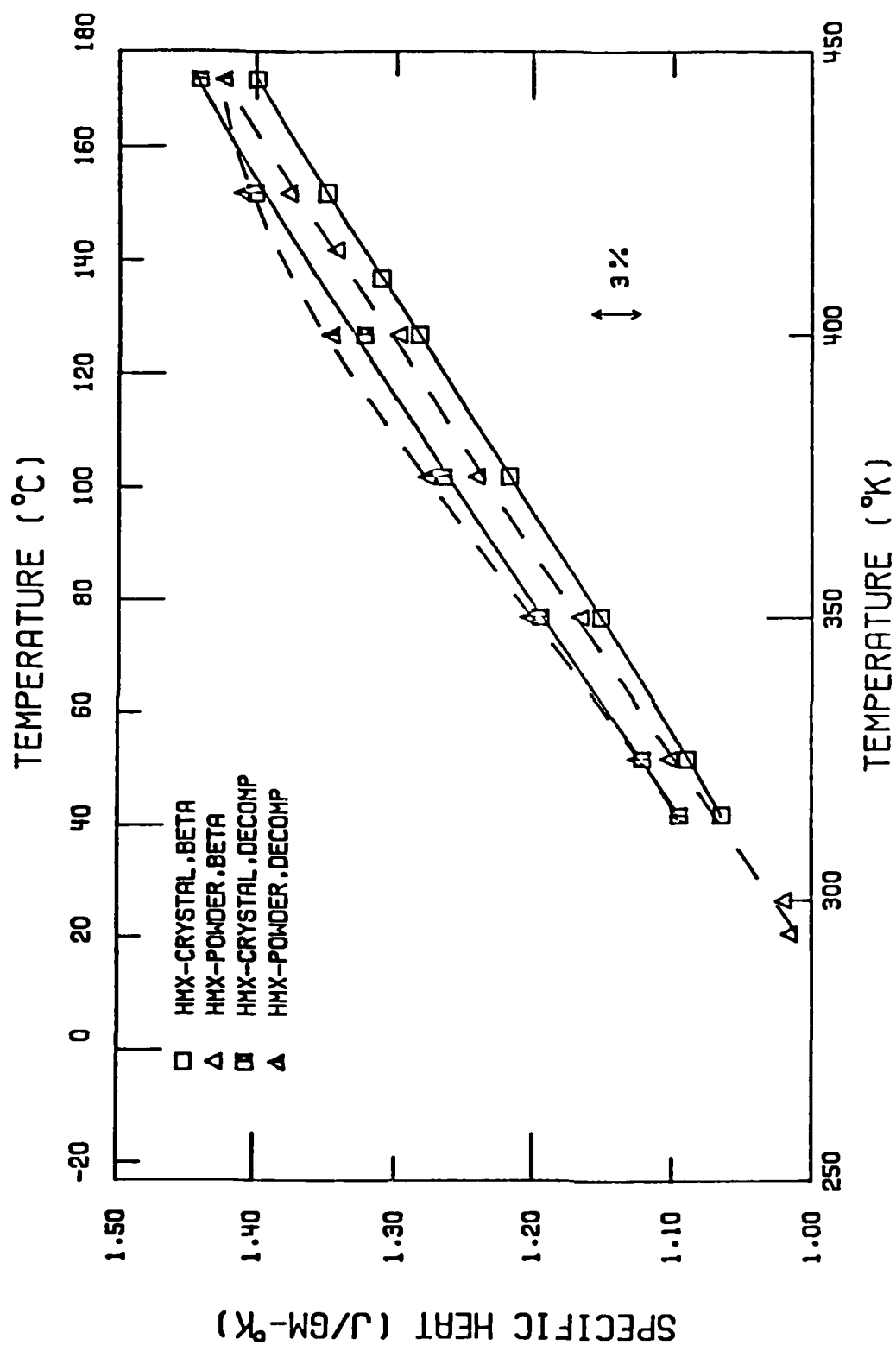Figure 3. Specific heat of single crystal and powdered blend delta HMX against literature results.

Figure 4. Specific heat of single crystal and powdered blend beta-HMX and partially decomposed HMX

REFERENCES

(1) Velicky, R., Lenchitz, C., and Beach, W., "Enthalphy Change, Heat of Fusion, and Specific Heat of Basic Explosives," Picatinny Arsenal, Dover, NJ, Technical Report 2504, Jan. 1959.

(2) Krien, G., Licht, H.H., and Zierath, J., "Thermochemische Untersuchen An Nitraminen," Thermochim. Acta, Vol. 6, 1973, pp. 465-472.

(3) Rylance, J., and Stubley, D., "Heat Capacities and Phase Transitions of Octahydro - 1,3,5,7 - Tetranitro - 1,3,5,7 - Tetrazocine (HMX)," Thermochim. Acta, Vol. 13, 1975, pp. 253-259.

(4) Wilcox, J.D., "Differential Scanning Calorimetry Methods in the Determination of Thermal Properties of Explosives," Air Force Institute of Technology, Air University, Wright-Patterson Air Force Base, OH, Master of Science Thesis, GAW/ME/ 67B-3, June 1967.

(5) Brill, T.B. and Karpowicz R.J., "Solid Phase Transition Kinetics: The Role of Intermolecular Forces in the Condensed Phase Decomposition of Octahydro - 1,3,5,7 - Tetranitro - 1,3,5,7 - Tetrazocine (HMX)," J. Phys. Chem., Vol. 86, 1982, pp. 4260-4265.

(6) Boggs, T.L., Price, C.F., Zurn, D.E., Derr, R.L., and Dibble, E.J., "The Self-Deflagration of Cyclotetramethylenetetranitramine (HMX)," AIAA/SAE 13th Propulsion Conference, Orlando, Florida, July 11-13, 1977.

(7) Karpowicz, R.J. and Brill, T.B., "The $\beta \rightarrow \delta$ Transformation of HMX: Its Thermal Analysis and Relationship to Propellants," AIAA J., Vol. 20, 1982, pp. 1586-1591.

(8) Teetsov, A.S. and McCrone, W.C., "The Microscopial Study of Polymorph Stability Diagrams," Microsc. Cryst. Front., Vol. 15, Nov. - Dec. 1965, pp. 13-29.

(9) Hall, P.G., "Thermal Decomposition and Phase Transitions in Solid Nitramines," Trans. Farad. Soc., Vol. 67, 1971, pp. 556-562.

(10) Cady, H.H. and Smith, L.C., "Studies on the Polymorphs of HMX,"
      Los Alamos Scientific Laboratory, Los Alamos, NM, LAMS-2652,
      May 1962.

(11) Koshigoe, L.G., Shoemaker, R.L., and Taylor, R.E., "Specific Heat
      of Octahydro – 1,3,5,7 – Tetranitro – 1,3,5,7, – Tetrazocine (HMX),"
      Thermophysical Properties Research Laboratory, Purdue University,
      West Lafayette, IN, TPRL 314, Jan. 1983.

APPENDIX I

SPECIFIC HEAT VALUES FOR SINGLE CRYSTAL AND POWDERED BLEND
β-HMX AT VARIOUS HEATING RATES

TEMP. ($°K$)	TEMP. ($°C$)	C_p (J/g$°K$) HMX-Single Crystal β Phase			C_p (J/g$°K$) HMX-Powdered Blend β Phase		
		2.5$°K$/min	5$°K$/min	10$°K$/min	2.5$°K$/min	5$°K$/min	10$°K$/min
315	42		1.065	1.049	1.084	1.072	1.063
320	47	1.054	1.078	1.062	1.099	1.085	1.076
325	52	1.065	1.089	1.074	1.115	1.102	1.089
350	77	1.122	1.152	1.136	1.149	1.166	1.158
360	87	1.147	1.177	1.162	1.172	1.191	1.188
375	102	1.189	1.217	1.200		1.241	1.232
400	127	1.275	1.284	1.269		1.299	1.297
420	147		1.337	1.318		1.359	1.341
425	152		1.349	1.332		1.376	
445	172		1.399	1.384		1.423	

APPENDIX II

SPECIFIC HEAT VALUES FOR SINGLE CRYSTAL AND POWDERED BLEND δ-HMX
OBTAINED IMMEDIATELY FOLLOWING THE β to δ TRANSFORMATION
AND ALSO OVER THE EXTENDED RANGE

T(°K)	T(°C)	C_p (J/g°K) HMX-Single Crystal δ Phase		C_p (J/g°K) HMX-Powdered Blend δ Phase	
		After Transition	Extended Range	After Transition	Extended Range
410	137		1.315		
415	142		1.330		1.347
425	147		1.362		1.381
450	177		1.411		1.439
472	199			1.461	
475	202		1.448		1.502
476	203			1.475	
477	204	1.443			
480	207	1.450		1.491	
483	210	1.458			
484	211			1.503	
485	212		1.470		1.524
486	213	1.465		1.506	

APPENDIX III

SPECIFIC HEAT VALUES FOR PARTIALLY DECOMPOSED SINGLE CRYSTAL
AND POWDERED BLEND HMX

$T(°K)$	$T(°C)$	C_p (J/g°K) Single Crystal Partially Decomposed	C_p (J/g°K) Powdered Blend Partially Decomposed
315	42	1.095	1.095
325	52	1.122	1.126
350	77	1.194	1.203
375	102	1.265	1.278
400	127	1.323	1.347
425	152	1.401	1.410
445	172	1.440	1.423

APPENDIX III

SPECIFIC HEAT VALUES FOR PARTIALLY DECOMPOSED SINGLE CRYSTAL AND POWDERED BLEND HMX

$T(°K)$	$T(°C)$	C_p (J/g°K) Single Crystal Partially Decomposed	C_p (J/g°K) Powdered Blend Partially Decomposed
315	42	1.095	1.095
325	52	1.122	1.126
350	77	1.194	1.203
375	102	1.265	1.278
400	127	1.323	1.347
425	152	1.401	1.410
445	172	1.440	1.423

ACKNOWLEDGEMENTS